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RECENT DEVELOPMENTS IN HIGH TEMPERATURE SUPERCONDUCTING MATERIAL RESEARCH

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ABSTRACT

The availability of high temperature (above liquid nitrogen temperature) superconducting materials can have an enormous impact on the power system. This report summarizes recent breakthroughs in high temperature superconducting materials research. Published papers in respected scientific journals relating to the fabrication, characterization and properties of several superconducting materials have been reviewed. The evidence shows unambiguously that macroscopic quantities of certain types of oxides can be made to superconduct at 77 K or above with an electrical resistivity of less than 3×10^{-8} Ω-cm, a factor of 100 lower than the resistivity of aluminum at room temperature.

INTRODUCTION

Recently there have been many reports about the discovery of superconducting materials with transition temperatures exceeding the liquid nitrogen boiling temperature of 77 K (-196 C). The applications of superconducting materials to the power system (eg. low loss power transmission, compact power generator, energy storage, and other devices) have previously been examined, and the hurdle for large scale application is the requirement for low temperature (liquid helium temperature of 4 K). The availability of high temperature superconducting materials can completely change the techno-economic picture, and will have an enormous impact on the power system.

This report summarizes the rapid advances in superconducting research during the past several months. Special emphasis is placed on differentiating newspaper reports, which often tend to be overly optimistic, from published scientific evidence. Papers published in recognized scientific journals relating to the fabrication, characterization and properties of several types of high temperature superconducting materials have been reviewed. The scientific evidence is assessed with particular attention to the practical application of the materials. Because of the large number of applications, this report will restrict the discussion to recent developments. A separate report on the possible applications of the new materials and the economic impact is being prepared and will be issued shortly (provided that there is no major development, such as the discovery of room temperature superconducting materials).

job	file	date	report no.
740615-542	811.4	April 3, 1987	87-102-K

SUPERCONDUCTING MATERIAL DEVELOPMENTS

The phenomenon of superconductivity was discovered in 1911 when scientists found that mercury lost its electrical resistivity at 4 K (-269 C) [1]. In the past seventy five years, the search for superconducting materials with high transition temperature has become one of the key research areas in solid state and low temperature physics. The highest transition temperature materials discovered were niobium-germanium and niobium-tin which were the design materials for superconducting cables and superconducting generators. Although these materials have a transition temperature of 23 K which exceeds liquid hydrogen temperature, their applications still involve expensive cryogenic equipment operating at the liquid helium temperature. The combination of high capital cost (mostly from refrigeration equipment) and high operating cost (from cooling) is the major hurdle for wide spread applications of superconducting materials. At present, superconducting materials based on the liquid helium economy are applied in specialized areas such as superconducting magnets for scientific investigations.

RECENT DEVELOPMENTS

The first hint of major breakthroughs in high temperature superconductivity research appeared in a paper published by J.G. Bednorz and K.A. Muller of the IBM Zurich Research Laboratory [2]. The metallic oxygen-deficient compound in the form of a Ba-La-Cu-O system (barium lanthanum copper oxide), with the composition $Ba_xLa_{(5-x)}Cu_5O_{5(3-y)}$ has been prepared in polycrystalline form. Samples with x=1 and 0.75, y>0 , annealed below 900 C under reducing conditions were found to show a loss of electrical resistivity of three orders of magnitudes in the 30 K range. The work is significant because it shows certain phases of the oxide compound can superconduct while previous research shows only a small number of oxides to exhibit superconductivity. This pioneer work pointed the direction of superconducting research to investigate oxide materials with various kinds of dopings.

Since the publication of Bednorz and Muller's paper in September 1986, various laboratories in the world have reported similar phenomena with higher superconducting temperatures. Bednorz and Muller's Ba-La-Cu-O system was shown to withstand a high magnetic field in the superconducting state. Takagi in Japan attributed the observed superconductivity in the Ba-La-Cu-O system to a special phase structure of the compound [3]. By increasing the pressure on the Ba-La-Cu-O system, M.K. Wu and C.W. Chu of the University of Alabama and University of Houston were able to raise the transition temperature to above 40 K [4]. By the replacement of Ba with Sr (strontium), B. Batlogg and co-workers at AT&T Bell Laboratories reported the bulk superconductivity phenomenon at 36 K in La-Sr-Cu-O with a narrow transition width of 1.4 K [5]. The associated dc diamagnetic susceptibility (Meissner effect) is close to that of an ideal superconductor. In February 1987, the properties and characteristics of the La-Ba(Sr)-Cu-O systems were investigated by many other groups including the low temperature physics group at McMaster University' Physics Department headed by J.P. Carbotte and T. Timusk [6].

The highest transition temperature was reported in a paper by Wu and Chu which appeared in the March 2nd issue of the Physical Review Letters [7,8]. The authors reported that a stable and reproducible superconductivity transition between 80 and 93 K has been unambiguously observed both resistively and magnetically in a new Y(Yttrium)-Ba-Cu-O compound at ambient pressure. The reported formulation of the compound is $(Y_{0.6}Ba_{0.4})_2CuO_4$. Figure 1 shows the temperature dependence of resistance of the YBCO material at various magnetic field strengths. The onset of transition temperatures stays above 77 K even in magnetic fields as high as 5.7 tesla. The temperature dependence of resistance at pressures of 0 kbar to 19 kbar is shown in Figure 2. The small effect of pressure on the transition temperature is a key re-

quirement for its applications. The discovery of transition temperatures above liquid nitrogen temperature of 77 K represents one of the greatest triumphs of scientific endeavour of this kind. C.W. Chu filed a patent application in the U.S. on 12 January, 1987.

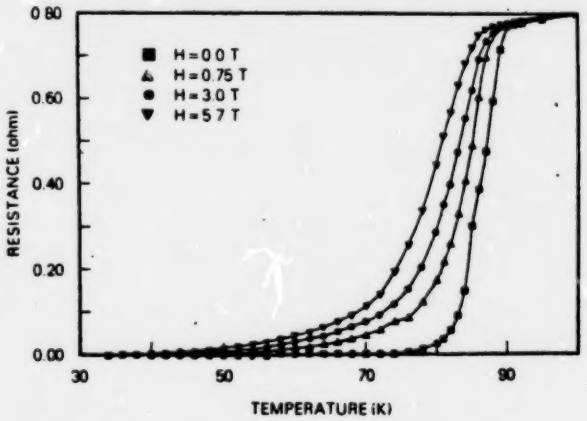

FIG. 1. Temperature dependence of resistance determined in a simple liquid-nitrogen Dewar.

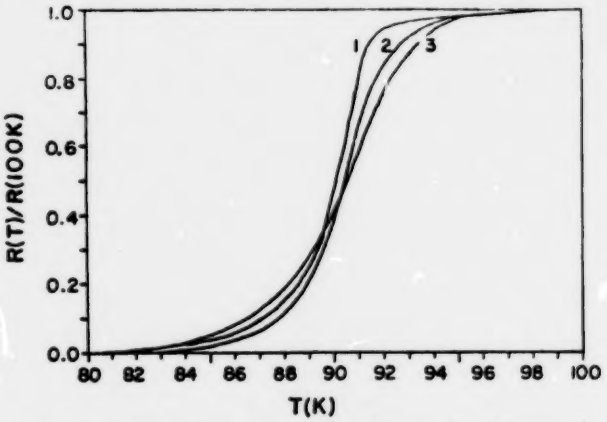

FIG. 2. The temperature dependence of resistance at different pressures: 1 = 0 kbar, 2 = 8.4 kbar, and 3 = 19 kbar.

Since the announcement of the discovery of superconducting materials above liquid nitrogen temperatures, there have been several reports in the newspaper about the discovery of materials at even higher transition temperatures. The latest reported discovery is 115 K in the $Y_{0.9}Ba_{0.1}CuO_3$ compound [9]. However, these reports were largely unconfirmed and their properties are unknown during the time of the preparation of this report. During the American Physical Society meeting in New York on March 18, there was an all night meeting attended by more than three thousand physicists to discuss the recent advances and their significance. All agreed that the recently discovered materials do indeed exhibit all the properties of high temperature superconducting materials. There are eight materials which reportedly have transition properties at higher than liquid nitrogen temperatures [6]. Detailed report of this meeting is attached in Appendix 1.

MATERIAL CHARACTERISTICS & CONDUCTION MECHANISMS

Because the discovery of these high temperature materials is very recent, there is little information about the materials' characteristics for an assessment about their practical application in the power system. Based on published information, the characteristics of these materials are discussed in the following paragraphs.

All the new superconducting materials are in a form of $L_{1-x}M_xA_bD_y$. Almost all the materials are in the form of copper oxide with barium and other elements. The variation of the doping elements (L and M) appears to have an effect on the transition temperatures. The Y-Ba-Cu-O system has a resistivity of less than 3×10^{-8} Ω-cm in the superconducting state. This resistivity is about 100 times less than the

resistivity of aluminum at room temperature. The compound was fabricated with nominal compositions through solid state reaction of appropriate amounts of Y_2O_3, $BaCO_3$ and CuO [7]. The ingredients were heated in a reducing oxygen atmosphere of 2×10^{-5} bars at 900 C for several hours. The process was repeated after pulverizing the reacted mixture. The reacted mixture was then pressed in cylinders for final sintering at 925 C for 24 hours in the same reducing oxygen atmosphere. Macroscopic samples of 1 x 1 x 3 mm were cut from the cylinders for resistance measurements in the Dewar. The standard 4-probe technique was used for the resistivity measurement. Preliminary x-ray diffraction analysis showed the existence of multiphase structures in the sample. It is not clear which phase is responsible for the superconducting state of the material. The oxide material is similar to a ceramic material which differs from metal in some material properties such as ductility.

The mechanism of superconductivity has been explained by the BCS theory (Bardeen Cooper and Schrieffer) [10]. Conduction electrons in superconducting materials are coupled in pairs via the electron-phonon (lattice vibration) interaction below the transition temperature. The existence of the Cooper pair greatly modifies the properties of the conduction electrons which are responsible for the loss of resistance. Based on the evidence collected about the properties of the new superconducting materials, scientists have not been able to satisfactorily explain the conduction mechanism. While it is tempting to attribute the superconducting phenomenon to possible non-conventional superconducting mechanisms, all present suggestions are considered tentative at best, especially in the absence of detailed structural information about the phases in the sample. The physics community is presently engaged in the search for a satisfactory theory to explain this new phenomenon.

OUTLOOK

The change of a liquid helium based superconducting technology and economy to a liquid nitrogen based economy can completely change the conclusions of all previous application studies. In addition, the lowering of the operating cost from LHe to LN_2 can lead to many new applications. Applied scientists have already made the first LN_2 thin film superconducting device for fast computer applications. Such a device involves the deposition of thin layers of the new superconducting material on a substrate for making a fast switching junction. In theory, room temperature superconducting material is possible and the basic conduction mechanism has been postulated as the exciton coupling mechanism to form the Cooper pair.

The application of high temperature superconducting materials to the power system will await detailed characterization of the material properties such as mechanical, electrical and magnetic properties. For example, acceptable current densities and magnetic field properties of the material may affect the current carrying capability. Furthermore the application of the new material to an industry in which reliability is most important may require further understanding of the basic mechanisms before an attempt is made for a large scale implementation. Organizations such as EPRI and BBC Research have already indicated interest in doing research in superconductivity.

The Research Division has an on-going interest in superconducting power transmission and other superconducting devices. Several reports have been prepared to discuss various types of cryogenic cables for underground power transmission [11,12]. Because of cooling requirements, all previous studies concluded that it was not economically viable to install superconducting devices in the power system. Recent advances in this field should open up possibilities of further research within the Division. Since the impact of this technology can be enormous, carefully evaluated scientific information is needed at various levels for decision making. Therefore the effort to keep aware of the technology should be up-

graded so that we can keep abreast of the rapid advancement. Although it is not inconceivable to carry out material fabrication and characterization research at the Division (the capital cost may not be as big as one might think), a less aggressive approach is to keep abreast of the advances and reexamine some of the previous application studies. The following are some approaches which the Research Division can consider:

1. Keep abreast of the technology by closely monitoring the advances. This may involve constant literature reviews of the scientific achievements, participation in conferences and workshops to gain up-to-date knowledge of the physics of superconducting mechanisms, characterization of material properties and fabrication techniques. These tasks should enable Hydro to gain first hand information about the technology for future application.

2. Re-examine some previous application studies and replace the economic modelling with models based on LN_2 or even dry ice temperature. These studies may lead to possible applications of significant benefits to Hydro but at a much reduced operating and capital cost.

3. Investigate new applications which can completely change the concept of power generation and delivery. Low voltage high current dc transmission and high energy density storage devices for system stability, and energy storage made possible by superconducting materials, are some of the examples.

CONCLUSIONS

Recent advances in high temperature superconducting material research have been reviewed. Based on the evidence presented in respected scientific journals, the existence of materials with transition temperatures well above liquid nitrogen temperatures of 77 K has been confirmed. The search for materials with higher transition temperatures is being pursued vigorously in the scientific community. While the mechanical properties of these new materials are not well established, preliminary investigation of the electrical and magnetic properties are not incompatible with applications in the power system. Close monitoring of the development in fabrication and characterization, and some application studies are recommended at this stage to keep abreast of this rapidly advancing technology.

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March 23, 1987

Dear Dr. Chu,

The March meeting of the American Physical Society had a special evening meeting on high temperature superconductors full of excitement as the various laboratories presented their latest results in what has become a big horse race. Every group had a five minute time slot, a real limitation considering that in some cases the work of some fifty collaborators had to be presented. I would like to tell you about some of the highlights of a session that started at eight in the evening and ended after three A.M.

The first speaker was Müller who with Bednortz at IBM Zürich had set out deliberately some two years ago to search for high temperature superconductivity among the oxides of Cu and Ni.

Next the Tokyo group told of their discovery of the LaSrCuO system. They were the first to give the big news at the meeting: the formula for the the superconducting component mystery "green stuff" of Paul Chu of the University of Houston, as written up in Time magazine. It turns out that ingredient in the green mess that counts is the oxide $Y_1Ba_2Cu_3O_{7-\delta}$, the 123 oxide, and it is not green but black. This formula had been discovered by many groups in a hectic race in the previous three weeks (John Greedan at McMaster had also made the 123 oxide independently just before the formula became widely known). The Tokyo group also listed other superconductors with transition temperatures in the high 85 -- 90 K range.

Compound	T_c	
$ScBa_2Cu_3O_{7-\delta}$	93	False rumor of 240 K T_c
$TmBa_2Cu_3O_{7-\delta}$	92	
$ErBa_2Cu_3O_{7-\delta}$	90	
$HoBa_2Cu_3O_{7-\delta}$	85	Magnetic RE
$DyBa_2Cu_3O_{7-\delta}$	85	Magnetic RE
$YbBa_2Cu_3O_{7-\delta}$	83	Magnetic RE
$YBa_2Cu_3O_{7-\delta}$	95	The original Chu material
$EuBa_2Cu_3O_{7-\delta}$	96	A very sharp transition

The particular rare earth does not seem to matter much. It was shown later that the current is carried on copper and oxygen chains that are far from the rare earth. (The Globe and Mail

reported on March 19 that Japan's MITI is already starting a 'study' of high T_c superconductors.)

The next speaker was Paul Chu who told us that the green phase in his mystery oxide was Y_2BaCuO_5, an insulating oxide. In the black phase he had seen "onsets" of superconductivity up to 160 K and "drops" of resistivity at 240 K. This later figure was also brought up by the Berkeley group but was received with some skepticism by the audience. The black compound is a layer structure and he suggested the superconductivity is of an excitonic type with excitons coupling layers of current carrying copper-oxygen chains. The 123 compound has the $A_6B_6O_{14}$ structure.

The next speaker was Bertran Batlogg of AT&T Bell Labs. They have a very large effort in this field. The 123 material has a resistivity just above the superconducting transition of 250 μΩcm and rises linearly to 750 μΩcm at room temperature. The Meissner effect is 76% of perfect diamagnetism (at McMaster we have found close to 100% diamagnetism indicating that the whole sample is superconducting).

Crucial to practical applications of superconductivity is the value of the critical current, the maximum current that the material will tolerate. Batlogg reported 1000 amperes/cm² and an upper critical field of 2 megagauss (200 tesla). He said that with currently measured properties a magnet could in principle be made with a 20 tesla field operating in liquid nitrogen. How do we make such a magnet out of a ceramic? This is where Batlogg pulled out an actual magnet wound with some kind of a wide ribbon. He said the ribbon contained a "green" unfired ceramic of the 123 oxide on a flexible backing. It will turn brittle on firing and to demonstrate it he held up a 3 inch square of the fired ceramic and a transparency showed a superconducting transition at 93 K. While his showmanship was faultless it should be pointed out that he had not in fact made a working magnet. Remaining problems are the making of contacts to the wire, including a stabilizing normal metal matrix, and providing an insulator between the turns that has to fired in the same structure as the superconductor.

I will skip the theoretical presentations. It is too soon to speculate on the mechanism of superconductivity in these materials. The opinion seems to be divided on the issue of new mechanisms. It is still possible that the superconductivity that we see here is of the old BCS type.

During the EXXON presentation it was established that the oxides of Ni^{+++} and Al^{+++} had been tried without success and that too high a firing temperature turns the 123 mixture green. For superconductivity, that is the black oxide a firing temperature of 900°C is best followed by an oxygen treatment at 500°C and slow cooling.

Laura Greene of Bell Communications gave the lattice constants of the 123 as a = 3.827, b = 3.877, c = 11.708. She also reported on single crystals as did others but nobody was forthcoming with any detailed information except to say it was some flux growth technique. She also said that the material is very stable at room temperature.

The University of Pennsylvania presentation discussed thermopower. It has the sign of hole conductivity and is quite large, 15 - 30 $\mu V/K$ in the normal state and goes away below the superconducting transition as it should. He reported that neutron irradiation increases the critical current.

Zack Fisk (wearing a very becoming fish tie) of Los Alamos showed results on Eu and Gd versions of the 123 material. The gadolinium was particularly interesting since it is magnetic.

The Stanford group had a very large program and were trying to prepare thin films in an attempt to do tunnelling measurements. IBM reported a 40 nm superconducting film done by multiple gun sputtering.

Zettl of the Berkeley group got into hot water earlier for announcing 240 K structure to the local press and like his state ex-governor did not come clean: "In view of the history of this subject I would like to point out structure at 240 K". This observer, seated close to the front in fourth row, could not discern the structure. Zettl had estimated the resistivity of the material in the superconducting state to be less than 10^{-17} Ωcm.

Some of the best was saved for the last. The McMaster group with their Florida collaborators presented the only optical conductivity data for the LaSr compound. It has a plasma frequency of 6500 cm^{-1} and a very interesting electronic absorption at 13000 and 5000 cm^{-1}, perhaps a charge transfer band. The existence of such a band is very important for some of the theoretical models. They also gave value for the energy gap consistent with the BCS theory. Most other gaps reported were either too low to make sense (Cornell, Berkeley, IBM, or too high, typically tunnelling results).

The Orsay group presented results on Josephson tunnelling consistent with $2e^-$ charge carriers showing that we still have paired electrons. This phenomenon is used in several practical superconducting electronic devices notably ultrasensitive magnetometers and voltage standards. The most important application is in ultra high speed computer elements. IBM reportedly spent 200 million on the Josephson computer before dropping the project recently.

The Karlsruhe group tried to sneak a very important discovery past the audience at this late hour. A 123 resistance curve with a very sharp transition at 120 K! On questioning it was revealed that the material had been heat treated in 2.5 bar of oxygen at 900°C and then again at 740°C. The times were not given. It appears from this that the optimum heat treatment is still to be found for this material and its ultimate capability has not yet been demonstrated.

The evening session made the front page of the New York Times again and more excitement has been promised.

Best regards,

Tom Timusk

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